



# Approaches to the manufacture of layered nanocomposites

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## ABSTRACT

Clay–polymer nanocomposites, resulting from industrial research, have emerged as a new class of material because a low addition of clay in a polymer matrix causes dramatic improvement in mechanical and barrier properties. They represent the low volume fraction (<4 vol.%) end of the composition range. The question now is: what will emerge from attempts to explore the high volume fraction (>60 vol.%) end? Naturally occurring materials, such as nacre, show that a combination of a high platelet content in a polymer with a layered structure is strong and tough (4–10 MPa m<sup>1/2</sup>), even if the reinforcement, aragonite in this case, is inherently brittle (~1 MPa m<sup>1/2</sup>). This achievement of nature has inspired the synthesis of materials to mimic the nacre structure using high aspect ratio reinforcements of high elastic modulus such as smectite clay tactoids. Preliminary successes were based on layer-by-layer assembly methods and it will be interesting to find out whether sufficient order can be obtained in composites assembled by more rapid manufacturing pathways. We are interested in the factors affecting dispersion, orientation and intercalation of platelets and here we survey the strategies that have been adopted in order to create organized structures of layered nanocomposites.

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## 1. Introduction

An engineering material can earn no greater trust than to be given a structural role in a civil aircraft. The Boeing 787 (Fig. 1) contains 50% composite materials, mainly carbon fiber reinforced, in structural airframe components. The first carbon fiber composites were made at the Royal Aircraft Establishment, Farnborough, UK in 1963 so it has taken nearly 50 years for them to reach this stage. In contrast, the lead-time for an entirely new aircraft, Concorde was only 20 years. It is often said that development of new materials sets the lead-time for new technologies and that is why the ages of civilisation are named after materials; stone age, bronze age, iron age and age of silicon. Now that carbon fibre composites have become accepted, we ask the question: what will be the next class of new structural materials?

## 2. The market position for carbon fiber composites

The predicted market for carbon fibre composites is £12 billion by 2011; growth has been up to 10% per annum and some 40,000 tonnes of carbon fibre are produced annually. It is a mature market, made more secure by the fact that any object that is

to fly should be constructed from high strength and stiffness to weight ratio materials. The same argument applies to an object that is to be accelerated. The fuel consumed by the world's 600 million cars is mainly converted for acceleration and overcoming air resistance. A new generation of low carbon vehicles is appearing: 250 mpg cars are being prototyped (Fig. 2), some with carbon fibre composite shells. Herein lies a problem. Carbon fibre itself is expensive in money and energy. The fabrication of the composite is labour and capital intensive. Yet the success of low carbon vehicles in moderating climate change depends critically on rapid replacement of vehicle stock. These vehicles must be cheap if they are to diffuse quickly into the market so the question arises; will carbon fibre composites provide the most appropriate body shell material?

## 3. The emergence of natural fiber composites

Natural cellulose fibres such as hemp [1,2], flax [3,4], ramie [5] and wood [6] have been identified as attractive fillers for composites because they are cheap, renewable and offer high mass-specific properties due to their low density. Holbery and Houston [7] reviewed their automotive applications. When embedded in thermoplastic polymers they offer up to 2:1 modulus ratio and are being explored as short fibre reinforced composites [4,8,9]. Prototype body panels for cars have been built. Fig. 3 shows the 'Eco-Elise' with hemp reinforced composite body panels. Although these natural fibres are generally regarded as energy efficient and provide labour opportunities in countries of origin,

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**Fig. 1.** As much as 50 percent of the primary structure including the fuselage and wing of the Boeing 787 Dream Liner is made of composite materials. (Reproduced by kind permission of Boeing Commercial Aeroplanes.)



**Fig. 2.** VW 1000cc low carbon vehicle with carbon fibre composite shell that can deliver 250 mpg. (Reproduced by kind permission of Volkswagen.)

there are environmental issues such as competition with food crops, depletion of soil, nutrients and fertilizer, use of pesticides and herbicides to protect the plants. The variability of properties and yields with weather conditions also needs to be assessed.



**Fig. 3.** The Eco-Elise has solar panels on the roof to help power electrics and the composite in the body panels is reinforced by hemp (Reproduced by kind permission of Lotus Engineering.)

There is also a movement to explore polymers derived from natural plant oils that can be incorporated into vehicle construction as composites [10]. This might seem radical but it is hardly new. Ford [11,12] patented a car body structure of soy-derived polymer reinforced by steel tube in 1940. So there is once again today, as in the heady days of the 1960s when carbon fibre composites appeared on the scene, scope for radical approaches to new composites driven both by their inherent fossil carbon footprint and their contribution to low carbon transport.

#### 4. Polymer–clay nanocomposites

Exfoliated clays, notably montmorillonite were incorporated into polyamides to form the first polymer–clay nanocomposites in 1985 at the laboratories of Toyota Motor Corporation. They showed significant modulus and strength improvement. Since then, there has been an explosion of interest from academic and industrial communities. Their automotive applications may well occupy a place in the history of technology as a class of new material with the lowest lead-time because they were in production in timing belt covers within four years of discovery [13]. Okada and Usuki [14] charted their development. These materials can accept no more than 5 wt.% clay or the mechanical properties begin to deteriorate. As well as providing a new class of composite material in their own right, they have opened up some tantalising questions: what other uses might there be for natural minerals in new materials? A more specific question might be: what lies beyond 5 wt.% in the polymer–clay nanocomposite ‘system’?

This question leads us to think about ordering in the micro- and nano-structure of composite materials. The far end of the composition range ( $\sim 0.8$ – $0.95$  inorganic volume fraction) is closed to commercial exploration because it is presently not possible to order nano-platelets either as individuals or as tactoids at the speed and scale of a production environment. A long-term strategic goal is therefore to find manufacturing pathways to create structural order in platelet reinforced composites and hence mimic the layered structures found in mollusc shells as suggested by Vincent [15,16].

#### 5. Biomimicry of nacre

In choosing aragonite to make mollusc shells, nature made what today’s material scientists would call a poor choice. But the selection of calcium salts was based on availability and solubility and once chosen, extraordinarily complex nanostructures evolved to provide high stiffness (resulting from mineral volume fraction of 0.95) and high strength (180 MPa) resulting from a ‘bricks and mortar’ arrangement of aragonite and proteins [17]. If there were Grand Challenges in Materials Science, this aim, appropriately generalized to the full range of layered minerals and indeed to other matrices would probably be one of them.

Mother of pearl or nacre as found, for example, in the shell of the abalone consists of 1  $\mu\text{m}$  thick plates of aragonite with about 5% protein in the form of inter-platelet layers. Nacre in the inner lustrous region of molluscan shells has exceptional mechanical properties stemming from its organizational hierarchy [18]. The structure in Fig. 4 is from the blue mussel (*Mytilus edulis*). Recent studies of nacre suggest that mineral bridges connect adjacent aragonite tablets [19] providing slipping resistance [20] and that large aspect ratios and staggered alignment contribute to stiffness. It now appears that the tablets are themselves composed of a nano-structure of 32 nm aragonite grains and biopolymers [21,22]. This awareness has stimulated three research themes; (i) to understand the toughening mechanism, (ii) to apprehend the morphogenesis and (iii) to synthesize nacre-like materials.

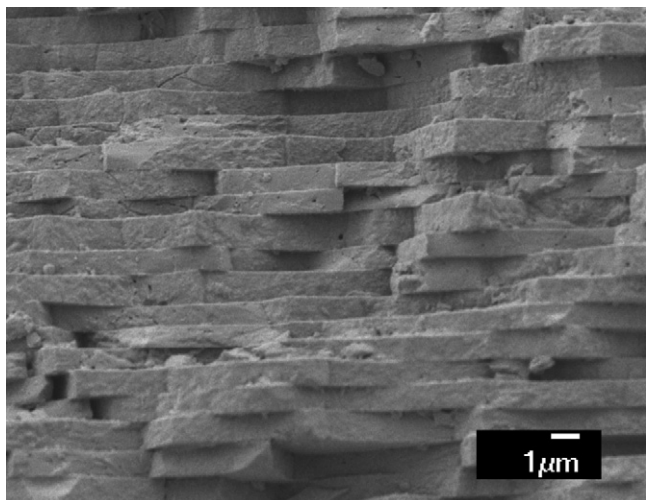


Fig. 4. The 'bricks and mortar' structure in the common mussel shell. (*Mytilus edulis*.)

The idea that a high modulus but brittle material can be toughened using a low modulus tough interlayer has, for a long time, been the basis of toughening float glass by lamination using polyvinyl butyral as adhesive [23]. A similar principle is at work in the toughening of high temperature materials by inserting thin, slightly porous interlayers to produce orthogonal crack deflection as pioneered by Clegg [24]. Thus the theme of this quest threads its way through the whole of materials science without regard to classes of materials.

Such composites fall into a different topological class in the Newnham contiguity-based taxonomy of composites [25] in which the designation is based on the number of dimensions in which each phase is contiguous. Thus while the powder-filled composite (0–3 in Fig. 5) provides restricted modulus enhancement based on volume fraction of reinforcement, the use of discrete fibres (1–3 composite) provides high unidirectional reinforcement and the woven fibre (2–3 composite) provides planar reinforcement. The layered clay nanocomposites would approximate to a planar 2–2 composite.

The particular challenge here is to apply this approach to assemble nano-scale mineral platelets but scaled up to make engineering composites. Of course, the energy absorption mechanism that contributes to toughness is different to that employed by fibre reinforced composites. Instead of a large contribution from fibre pullout, crack deflection along tortuous energy absorbing polymer-rich pathways contributes to toughness but the principle is the same; the mechanical properties are derived from the micro- and nano-structural arrangement.

## 6. Approaches to alignment

Almqvist et al. [26] attempted to make nacre-mimicking materials by introducing preferred orientation in concentrated talc suspensions through quite a few ways including sedimentation, centrifugation, spinning, shearing (in various configurations) and dipping. Talc tablets are several hundred nanometres thick and 3–10 μm across. The talc plates were found to be generally unidirectional but the structural ordering was not ideal at a microscopic degree.

Smectite clay platelets are over two orders of magnitude thinner, typically 1 nm in thickness. Recent work has been focused on this type of clay. The general approach is to start with an exfoliated clay colloid. Surfactants or mechanical force can be used to promote full exfoliation of clays in water [27] as can adjustment of

ionic strength and pH [28]. Above ~1 vol.% clay, the dispersion stiffens and becomes gel-like so the starting material needs to be very dilute. As long ago as 1994, Kleinfeld and Ferguson [29] produced ordered thin films of aligned hectorite platelets on silicon through a layer-by-layer (LBL) method.

Table 1 summarizes the physical methods to align the particles with a brief description and the corresponding sources; an extended description of selected methods follows.

Layer-by-layer deposition is a method adopted to form multilayered structures with nanometer-level control over the architecture based on alternate deposition of inorganic and organic layers. Tang et al. [30] produced composite layers of about 5 μm thickness through LBL deposition by alternately dipping a glass slide in polyelectrolyte and clay platelet suspension. Each cycle deposited only 24 nm and the cross section showed a wavy laminate of platelets. Podsiadlo et al. [31] extended this method and produced a homogeneous, optically transparent material with planar orientation of montmorillonite in poly (vinyl alcohol) nanosheets. It took a large number of dipping and drying steps to make a film of 1.5 μm thickness. The press reported "New plastic is strong as steel and transparent". Again, the layers were wavy which would tend to reduce the mineral volume fraction. The important message from the Michigan group is that elastic modulus reached 125 GPa and ultimate tensile strength reached 480 MPa which, notwithstanding the volume-dependence of failure stress (the test samples were very small), is high. This sends out a signal that the quest for a nacre mimic using smectite clays, possibly layered-double-hydroxides (LDHs) or even ceramic platelets such as alumina is sound and well worthwhile [32,33].

After further exploration in the same group, a thickness of 200 μm was prepared based on exponential growth of the layer thickness against dipping time due to the diffusion of the depositing polymer into the layer and then out of the layer while rinsing and subsequent deposition of clay [34]. Gauckler's [35] group at EHT Zurich have prepared alumina platelet reinforced chitosan by a modified LBL sequential deposition by assembling the platelets at water–air interface as a result of surface tension of water before deposition onto a surface.

Electrophoretic deposition is a simple and inexpensive technology that enables rapid production of films with adjustable thickness and geometries. It is based on the motion of charged particles under an applied electric field towards an electrode and has been used routinely to produce advanced ceramics since the 1970s [36]. Chan [37] and Zhitomirsky [38] discuss the issues, including mechanism of electrophoresis, effect of solvent on the dielectric constant and particle surface charge and electrode reactions. More recently, this method was applied to produce layered nanocomposites. This can be achieved in a range of ways: depositing clay into a layered structure followed by infiltration of the polymer/monomer [39], co-depositing the clay and polymer dispersed in the same solution [40], or depositing the emulsion made of clay–polymer composite particles [41]. A mixture of ethanol and water is commonly used as the solvent to reduce the repulsion of the platelets and favour coagulation and uniform deposition.

A similar layered structure of smectite clay has been obtained with considerably more experimental economy by drying of a clay suspension [42]. The clay was a calcium-rich montmorillonite so that by adjusting the sodium/calcium balance, the face-to-face attraction could be controlled. Chen et al. [27] used a centrifugal method to align platelets, in which a mixture of polyamide monomers and exfoliated montmorillonite were deposited by centrifugation onto a glass surface and subsequently polymerised to produce the composite. Furthermore, Park and Robertson [43] successfully applied an electric field to align particles with a variety of shapes from suspension. Platelets could be more rapidly aligned than fibres and other shaped particles. Alignment was distinct from



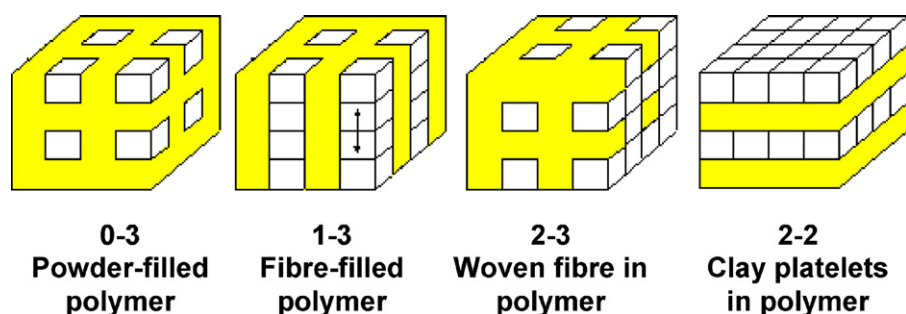


Fig. 5. A range of composites expressed in Newnham's taxonomy.

Table 1

Summary of methods to align particles into layered structures.

Method	Description	Sources
Layer-by-layer Deposition	Alternate deposition of inorganic and organic components to form a multilayered structure.	[30,31,34]
Electrophoresis	Charged particles move towards an electrode in an applied electric field and deposit onto the electrode.	[36,37,39,44]
Slip casting	A clay dispersion (slip) is poured into a plaster mould and forms a layer (the cast) on the internal surface of the mould. The layer dries by permeation of the solvent into the mould and subsequent evaporation.	[44]
Centrifugation/Sedimentation	Sedimentation of particles from a dispersion by gravity possibly enhanced in the centrifuge.	[26,27,44]
Drying	Progressive evaporation of dilute dispersions of platelets so that a layered structure is achieved.	[42,44]
Filtration	Filtration of a dispersion of platelets under vacuum to separate and align the particles.	[45,46]
Shearing	The platelets align in shearing direction.	[26]
Extrusion	Platelets align due to the induced shear when extruded.	[47]

movement: at higher fields, electrophoresis occurred and particles migrated to the electrode.

Liu et al. [44] in the authors' group explored five methods of platelet alignment including electro-deposition, sedimentation, centrifugation, slip casting and filtration in order to create layered structures of smectite clay. Similar methods have been used to align montmorillonite and synthetic Co–Al layered double hydroxides by the present authors. The stability of montmorillonite and LDHs in their aqueous suspensions can be largely affected by the pH of the suspension due to their permanent basal surface charge and pH sensitive charge at the edges. It was found montmorillonite suspension is stable at higher pH (above their isoelectric point) and LDH suspension is stable at lower pH (below their isoelectric point). Fig. 6 shows the layered assembly of montmorillonite at pH 11 obtained by simply filtrating its suspension, which is less than 100  $\mu\text{m}$  thick. In filtration methods, there is a limiting layer

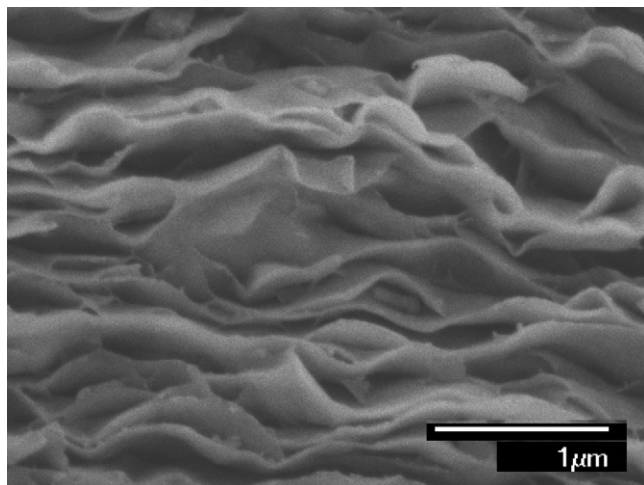


Fig. 6. Layered structures of montmorillonite tactoids produced by filtration.

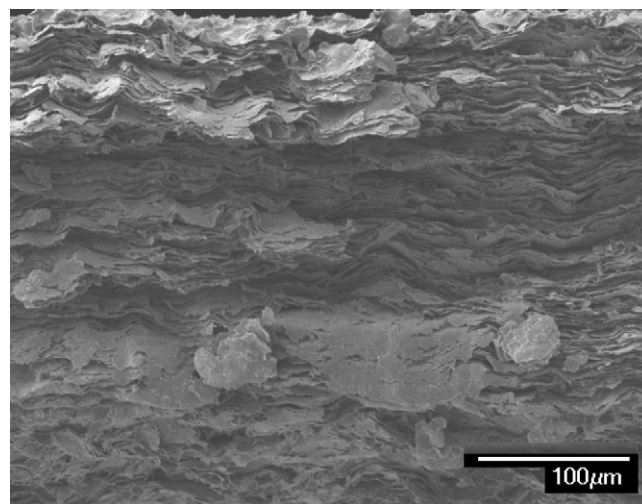


Fig. 7. Aligned Co–Al layered double hydroxide platelets produced by filtration.

thickness at which the flux of suspension and hence build-rate fall to zero. The use of LDH tactoids produces a thicker limiting layer than the use of exfoliated platelets. Fig. 7 shows a layered LDH structure of tactoid platelets more than 300  $\mu\text{m}$  thick at pH 4. It is possible to exfoliate LDH tactoids into single platelets that have high strength [48]. Further efforts are in progress to align these single platelets and to achieve thicker films.

## 7. Summary

Several groups around the world have realised that a new generation of composite materials may be just around the corner and that quite humble reinforcing constituents, namely clays, could play an important part in their construction. There is a need for high strength and stiffness to weight ratio composites for the emerging class of low carbon vehicles which, to succeed in their climate

change role, must penetrate the replacement market rapidly and therefore have modest cost. These new-layered nanocomposites may fulfil this need. They have one other advantage; all the indications are that they will not ignite.

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